

LETTERS TO THE EDITOR

Crystallinity in Drawn Fibers of Polyethylene Terephthalate

In a recent communication by Johnson¹ a good correlation was obtained between the crystallinity measured by x-ray diffraction and density on a number of polyethylene terephthalate yarns of different draw ratio. We have recently completed a large number of measurements^{2,3} of crystallinity on polyethylene terephthalate yarns using these two methods of measurement. With randomly oriented specimens a good agreement was found between the crystallinities measured by density and x-rays, but with the drawn yarns, under our conditions of preparation, no correlation was found to exist.

The x-ray method has been described in detail elsewhere.² Drawn fibers were chopped and made into a randomized sample by a pelleting technique similar to that of Hermans and Weidinger.⁴ The sample was placed on the circumference of a focusing camera (evacuated to eliminate "air scatter") and exposed to a strictly monochromatic beam of x-rays. The x-ray diffraction pattern was recorded on photographic film which, after processing and drying under standard conditions, was scanned by a microdensitometer. From the resultant trace the crystallinity was determined by measuring the integrated area of the noncrystalline background and the integrated area of the crystalline reflections and comparing the two in a manner similar to that used by Mathews et al.⁵ The scattering efficiencies of the crystalline and amorphous regions were assumed to be equivalent, and the correction of intensities for polarization, etc., were made in the normal way. The physical densities of the samples of yarn were measured by observing the point to which the samples sank in a graded density column.⁶

It had been assumed in our calculations, as had Johnson, that the amorphous material in partially crystalline drawn fibers of polyethylene terephthalate gave rise to the same x-ray reflection contour, but reduced in proportion, as that in a truly amorphous sample. Some experimental justification for this assumption was found from examination of traces of randomized samples of moderately oriented material (low draw ratio yarn 0-3.0, birefringences approximately zero to $\Delta = 150 \times 10^{-3}$) which showed very little or no crystallinity and comparing the contours with that obtained from an unoriented amorphous sample. Little difference in shape was found between these curves but in all these randomized drawn samples showing little or no crystallinity the density had increased from the value of 1.335 g./cc. usually found in an unoriented amorphous sample of polyethylene terephthalate. An example is given in Figure 1. Taking the x-ray measure of crystallinity as the yardstick and subtracting this figure from that obtained by density, a density value was obtained for these oriented noncrystalline regions. In most cases the value was near to 1.355 g./cc.

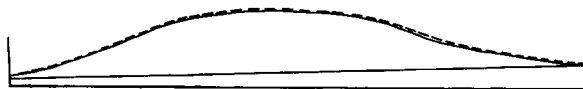


Fig. 1. Polyethylene terephthalate microdensitometer traces. Continuous line: Amorphous specimen, density = 1.335 g./cc. Discontinuous line: Low draw ratio (2.0) randomized yarn ($\Delta = 94 \times 10^{-3}$), density = 1.348 g./cc.

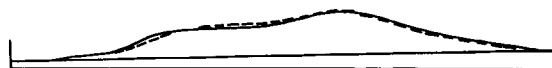


Fig. 2. Polyethylene methylterephthalate microdensitometer traces. Continuous line: Amorphous specimen, density = 1.170 g./cc. Discontinuous line: drawn "amorphous" yarn randomized ($\Delta = 60 \times 10^{-3}$), density = 1.199 g./cc.

Further evidence was adduced for this oriented noncrystalline material from examination of drawn fibers of poly(ethylene methylterephthalate) which we found impossible to crystallize. There was an increase in the birefringence and density with the drawn fibers, as was also found with the drawn fibers of polyethylene terephthalate. Details are given in Figure 2.

We, therefore, concluded from our measurements that no correlation existed between the crystallinity measured by x-ray diffraction and density in drawn polyethylene terephthalate fibers because the density of the amorphous material could no longer be considered constant at 1.335 g./cc.

References

1. Johnson, J. E., *J. Appl. Polymer Sci.*, **2**, 205 (1959).
2. Farrow, G., and D. Preston, *Brit. J. Appl. Phys.* in press.
3. Farrow, G., and I. M. Ward, *Polymer*, in press.
4. Hermans, P. H., and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948).
5. Mathews, J. L., H. J. Peiser, and R. B. Richards, *Acta Cryst.*, **2**, 85 (1949).
6. Kolb, H. J., and E. F. Izard, *J. Appl. Phys.*, **20**, 564 (1949).

G. FARROW

Research Department, Fibres Division
Imperial Chemical Industries Limited
Hookstone Road, Harrogate
Yorkshire, England

Received March 28, 1960